

# SPECTROSCOPIC CHARACTERIZATION OF VISBREAKING TAR

R. Scotti, M. Clericuzio, C. Pirovano

*Eniricerche S.p.A., via Maritano, 26 - 20097 San Donato Milanese (MI) - Italy*

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## INTRODUCTION

Visbreaking (VB) is a thermal cracking process, widely used in the refineries of Western Europe to obtain distillates (gasoil, naphtha) from a petroleum residue (feedstock). The visbroken residue (tar) is used to produce fuel oil, after addition of the appropriate amounts of cutter-stock.

Even if the highest conversion of feedstock would be desirable, the severity of the VB process is limited by the stability of the resulting VB tars. The stability index (SI) here employed is:

$SI = 1 + V_{\text{cet}}$ , where  $V_{\text{cet}}$  is the maximum amount of *n*-cetane, expressed as ml of cetane for g of sample, that can be added before the flocculation of asphaltenes starts. VB tars having  $SI < 1.1$  are considered to be unstable and cannot be used in the preparation of fuel oils with the appropriate specifications.

Several papers can be found in the literature dealing with the molecular changes occurring during the VB process [1-3]. The present paper is aimed at verifying the amount of information that can be extracted from optical spectroscopies and, in particular, the possibility of directly monitoring the physico-chemical modifications caused by VB process. To this purpose a series of VB tars, produced from a single feedstock at different severities, were investigated by a number of spectroscopic techniques, viz.: NIR; UV-Vis; Fluorescence;  $^1\text{H}$  and  $^{13}\text{C}$  NMR; EPR.

## EXPERIMENTAL

The lab visbreaking apparatus has already been described in detail elsewhere [4]. VB experiments were carried out in a continuous bench-scale unit under isothermal conditions (442 °C); the severity of the process was therefore determined only by residence times, varying from 3.5 to 9 minutes. The feedstock employed in the VB experiments was a 500°C + vacuum residue (VR) produced from a mixture of different crudes. VB tars were produced after distillation at 350 °C (350+, atmospheric pressure) or at 500 °C (500+, under vacuum). Asphaltenes were separated according to the IP 143 method. Deasphalted oil (DAO) was fractionated into saturate, aromatic and polar components via liquid chromatography according to a partially modified ASTM D 2549 method, using *n*-hexane, *n*-hexane/toluene, chlorophorm/diethylether/ethanol as eluents. The feedstocks were also characterized in terms of elemental analysis (ASTM D5291), total sulphur (ASTM D1552), Conradson Carbon Residue (CCR, ASTM D5430), specific gravity (ASTM D4052) and viscosity, measured at 50 and 100 °C by a RMS 800-Rheometrics.

Near-Infrared spectra were collected on a Guided Waves model 260, UV-Vis spectra on a diode-array Hewlett-Packard 8452A spectrophotometer.

Fluorescence spectra (corrected both in excitation and in emission using the standard Perkin-Elmer procedure of the instrument) were recorded on a Perkin-Elmer MPF-66 spectrofluorimeter.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-300, operating at 300.130 MHz for proton and 75.470 MHz for carbon.  $^{13}\text{C}$  quantitative spectra were obtained using an Inverse Gate decoupling technique.  $\text{CDCl}_3$  was used as solvent.

EPR spectra were recorded on a Bruker ESP 300 E operating at X-band (9.5 GHz). Strong pitch ( $3 \times 10^{15}$  spin/cm  $\pm$  15%) was used as quantitative reference.

## RESULTS AND DISCUSSION

The physico-chemical properties of feedstock, VB tars, and the fractions obtained from 350+ tars are reported in tabs. 1, 2 and 3, respectively.

The molar ratio of aromatic carbon ( $F_w$ ) and the main lengths of side chains (*n*) were calculated by NMR analysis, according to Dickinson [5,6].

A general increase of  $F_w$  and of asphaltene content with increasing VB severity is evident (tabs. 2-3). From the analysis of tar fractions (tab. 3) it turns out that the increase in  $F_w$  and the decrease in *n* mainly occurs in asphaltenes. This is in agreement with previous studies of the molecular effects of VB [2]: at relatively low severity asphaltene dealkylation occurs via breaking of aliphatic side chains, dehydrogenation and ring-opening of naphthenic moieties occurs, leading to more aromatic structures.

The relative amount of radicals (from EPR) increases with VB severity (tab. 2). *g* factors are not significantly affected by thermal treatment within each series. These radicals are associated with non-localized  $\pi$  systems stabilized by resonance over polyaromatic centers [7]. The slight difference between 350+ and 500+ tars ( $g_{350+} = 2.0026 \pm 0.0001$ ;  $g_{500+} = 2.0029 \pm 0.0001$ ) could be assigned to the different content in heteroatoms of the two series.

The electronic absorption spectrum of a typical VB tar shows a broad and unstructured band spanning the UV and visible regions of the spectrum, with absorption maxima around 260-270 nm (data not shown). For each sample the extinction coefficient  $\epsilon_w = A/c$  ( $c$  expressed as w/v) was calculated as the slope of the straight line fitting the absorbances at 0.1, 0.05, 0.025, 0.0125 mg/ml in  $\text{CCl}_4$ . The use of w/v concentrations, rather than molar, is justified by the critical values of average molecular weights in heavy petroleum derivatives, owing to association phenomena [8].  $\epsilon_w$ , obtained at 280 and 320 nm, increases with increasing VB residence time within each of the two series, 350+ and 500+ (fig. 1, only 500+ shown). This is in agreement with the increase of aromatic chromophores.

Fluorescence spectra were recorded both in THF and  $\text{CCl}_4$  solutions (0.0125 mg/ml).

The excitation spectra show, in both solvents, two main maxima, centered at about 330 and 390 nm (data not shown). Emission spectra were recorded with excitation centered at 394 nm: in THF a maximum in emission is observed at 453 nm (fig. 2, top). In fig. 3 emission intensities at 453 nm (in THF) are plotted for the eight samples: they show an increase with increasing VB severity in both series, which is related to the increase in aromaticity.

Spectra recorded in  $\text{CCl}_4$  are markedly different (fig. 2, bottom). The overall intensity is approximately 4-fold smaller in  $\text{CCl}_4$  than in THF, and maxima in emission are red-shifted about 25 nm. This clearly shows that in  $\text{CCl}_4$  VB tars are much more aggregated: in fact, formation of molecular complexes is expected to lead to fluorescence quenching and red-shifted emissions. Molecular association is a well-known phenomenon in the chemistry of asphaltenes, even at very low concentrations [8-9]. Our explanation is that the polar THF is more effective in disrupting the aggregation state of VB tars.

An interesting phenomenon is observed when fluorescence spectra are recorded in  $\text{CCl}_4$ . Immediately after the solution is prepared, the intensity of the spectrum decreases gradually with time until a plateau is reached, generally within one hour (fig. 4). The phenomenon is partially reversible after stirring the solution, and is much less evident in THF. Slow diffusion phenomena in solution, or a simple sedimentation effect might be responsible for this. NMR-Imaging studies are in progress to have more information.

An analogous phenomenon is observed in the NIR spectrum. The freshly prepared solution in  $\text{CCl}_4$  (10 mg/ml) shows an increase of baseline with time (fig. 5), probably due to Rayleigh scattering. It is likely that rather large particles are formed.

To avoid changes in baseline, NIR spectra were recorded under stirring, using optical fibers.

The spectra show a broad continuum with increasing absorption at higher energy, which is attributed to electronic transitions of large aromatic ring systems [10], and a second region at lower energies, which is attributed to vibrational overtones and combination bands of predominantly saturated hydrocarbons [10]. The ratio between  $I_{1200}$  (electronic transitions) and  $I_{2300}$  (C-H stretch plus bend) increases with severity (fig. 6).

## CONCLUSIONS

- 1) Our data suggest that it is possible to monitor the severity of VB by means of optical spectroscopies (potentially also on-line). In fact UV and NIR absorption intensities, as well as fluorescence emission intensities, are all sensitive to the molecular changes occurring during the VB process.
- 2) The solvent has a marked effect on the solution structure of VB tars; in particular in  $\text{CCl}_4$ , as compared to THF:
  - a) solute molecules are in a higher aggregation state;
  - b) the equilibrium structure is reached rather slowly, and is at least partially reversible by stirring;
  - c) rather large particles are probably formed.

Care should therefore be taken in analytical applications when using  $\text{CCl}_4$  as solvent, otherwise the reproducibility of measures will be strongly affected.

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Table 1: Physico-chemical properties of feedstock

|                       |        |                    |      |                        |     |
|-----------------------|--------|--------------------|------|------------------------|-----|
| Specific gravity 15°C | 0.9896 | CCR wt%            | 14.3 | <i>Dist. fractions</i> | °C  |
| Viscosity 50 °C [cSt] | 30,800 | SI                 | 6.3  |                        |     |
| Viscosity 100°C [cSt] | 660    |                    |      | Initial Boiling Point  | 306 |
| H wt%                 | 10.9   |                    |      | 5 wt%                  | 434 |
| C wt%                 | 86.3   | C7-Asphaltenes wt% | 5.8  | 10 wt%                 | 478 |
| N wt%                 | 0.8    | DAO composition:   |      | 30 wt%                 | 563 |
| S wt%                 | 1.4    | Saturates wt%      | 25.4 | 50 wt%                 | 618 |
| V [ppm]               | 79     | Aromatics wt%      | 46.2 | 70 wt%                 | 680 |
| Ni [ppm]              | 58     | Polars wt%         | 22.6 | 90 wt%                 | 756 |

Table 2: Physico-chemical properties of 350°C+ and 500°C+ VB-tars

| Time [min] | SI  | Sp.Gr. | V. 50 [cSt] | V. 100 [cSt] | H/C  | N %wt | S %wt | Coke %wt | F <sub>w</sub> | N <sub>i</sub> x10 <sup>16</sup> |
|------------|-----|--------|-------------|--------------|------|-------|-------|----------|----------------|----------------------------------|
| 350 °C +   |     |        |             |              |      |       |       |          |                |                                  |
| 3.5        | 1.8 | 1.000  | 26,700      | 400          | 1.42 | 1.1   | 1.3   | 0.03     | 0.26           | 5.5                              |
| 5          | 1.5 | 1.004  | 30,100      | 450          | 1.40 | 1.1   | 1.3   | 0.04     | 0.29           | 6.8                              |
| 7          | 1.2 | 1.006  | 30,200      | 440          | 1.36 | 1.2   | 1.3   | 0.22     | 0.30           | 8.0                              |
| 9          | 1.1 | 1.008  | 31,200      | 470          | 1.36 | 1.2   | 1.3   | 0.40     | 0.32           | 8.5                              |
| 500 °C +   |     |        |             |              |      |       |       |          |                |                                  |
| 3.5        | 1.9 | 1.011  | 259,750     | 1,600        | 1.35 | 1.5   | 1.3   | 0.04     | -              | 6.5                              |
| 5          | 1.6 | 1.013  | 429,700     | 2,250        | 1.33 | 1.5   | 1.3   | 0.06     | -              | 6.7                              |
| 7          | 1.3 | 1.025  | 1,155,400   | 3,750        | 1.30 | 1.4   | 1.3   | 0.28     | -              | 10.8                             |
| 9          | 1.2 | 1.032  | 1,862,500   | 6,050        | 1.27 | 1.4   | 1.4   | 0.53     | -              | 12.9                             |

Time: residence time; SI: stability index; Sp.Gr: specific gravity at 15°C; V.50, V.100: viscosity at 50 and 100°C; F<sub>w</sub>: molar ratio of aromatic C by NMR; N<sub>i</sub>: spin density [spin/g] by ESR.

Table 3: Composition of VB-tars 350 °C +

| Time<br>[min] | SI  | Satur. | Aromatics |                |     |      | Polars         |     |      | Asphaltenes    |     |  |
|---------------|-----|--------|-----------|----------------|-----|------|----------------|-----|------|----------------|-----|--|
|               |     | wt %   | wt%       | F <sub>w</sub> | n   | wt%  | F <sub>w</sub> | n   | wt%  | F <sub>w</sub> | n   |  |
| 3.5           | 1.8 | 25.4   | 41.5      | -              | -   | 22.2 | -              | -   | 10.9 | 0.56           | -   |  |
| 5             | 1.5 | 25.7   | 40.3      | 0.35           | 6.1 | 22.4 | 0.42           | 5.3 | 11.6 | 0.62           | 4.7 |  |
| 7             | 1.2 | 24.2   | 36.6      | 0.33           | 5.9 | 26.4 | 0.45           | 5.5 | 12.8 | 0.67           | 4.2 |  |
| 9             | 1.1 | 24.0   | 36.9      | 0.34           | 6.2 | 25.5 | 0.44           | 5.3 | 13.6 | 0.68           | 3.7 |  |

Time: residence time; SI: stability index; F<sub>w</sub>: molar ratio of aromatic C by NMR; n: main length of side chains.

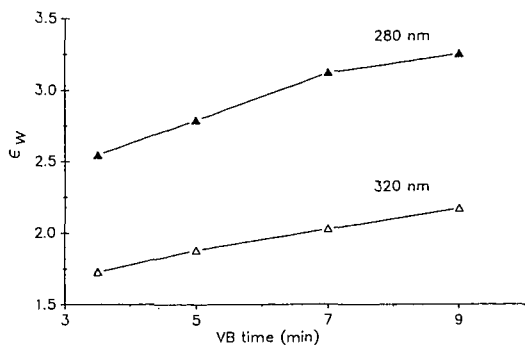


Fig. 1 - Extinction coefficients of 500+ tars (per gram) vs. VB severity.

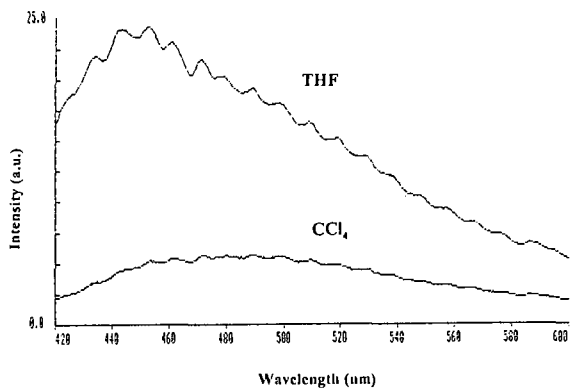


Fig. 2 - Fluorescence emission spectra of a selected VB tar. Excitation: 394 nm.

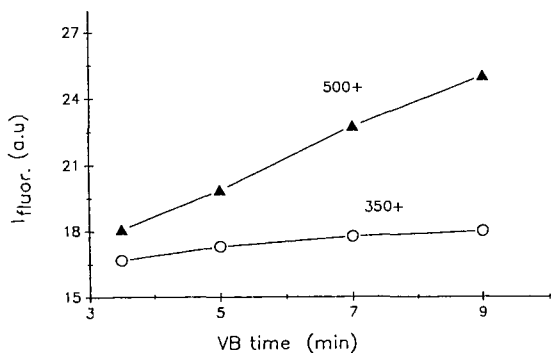


Fig. 3 - Intensity of fluorescence emission at 500 nm (exc. 394 nm) vs. VB severity. Solvent: THF.

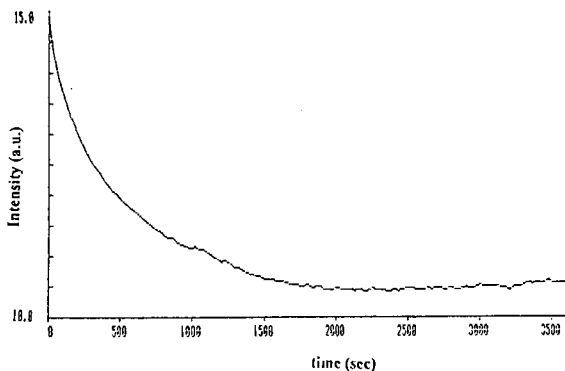


Fig. 4 - Time evolution of the intensity of fluorescence emission at 500 nm (exc. 394 nm). The solution is prepared by 1:100 dilution of an initial sol. in  $\text{CCl}_4$ .

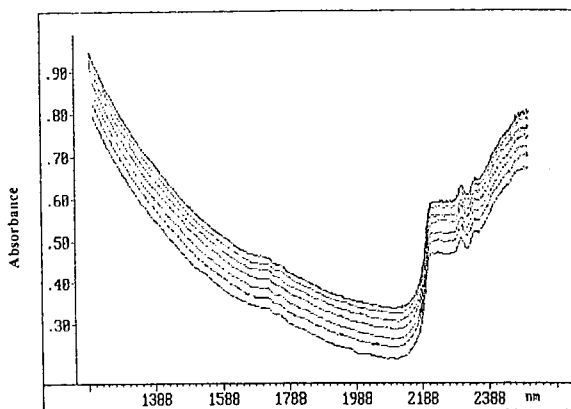


Fig. 5 - NIR spectra of a selected VB tar in  $\text{CCl}_4$ . Spectra were recorded every 8 minutes from 0 (bottom trace) to 48 min. (top trace).

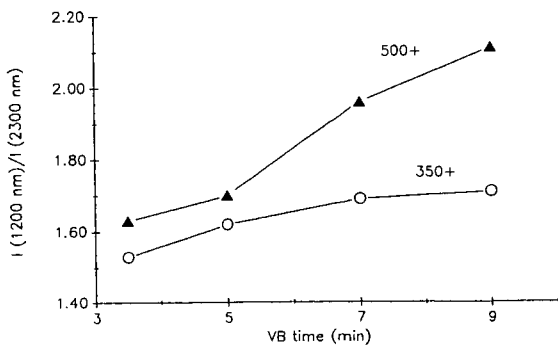


Fig. 6 - NIR intensity ratio between the bands at 1200 and 2300 nm vs. VB severity. Solvent:  $\text{CCl}_4$ .